Beyond paper: PFAS linked to common plastic packaging used for food, cosmetics, and much more

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Results from an [HYPERLINK "https://www.epa.gov/newsreleases/epa-takes-action-investigate-pfas-contamination"] into PFAS-contaminated pesticides have much broader, concerning implications for food, cosmetics, cleaning products, and other consumer products, as well as recycling. This investigation, first announced in January, found that fluorinated high-density polyethylene (HDPE) containers used for pesticide storage contained a mix of short and long-chain per- and polyfluorinated alkyl substances (PFAS), including [HYPERLINK "https://www.epa.gov/sites/production/files/2021-03/documents/results-of-rinsates-samples_03042021.pdf"], that leached into the product. From what EPA knows, t~~T~~he PFAS were not intentionally added to the HDPE but are hypothesized to have been ~~were~~ produced when fluorine gas was applied to the plastic.

The process of polyethylene fluorination was approved by the Food and Drug Administration (FDA) in 1983 for food packaging to reduce oxygen and moisture migration through the plastic that would cause foods to spoil. The fluorination process forms a Teflon-like barrier on the plastic's surface. It is also used to strengthen the packaging, although this use was not included in the FDA approval.

Since EPA released its investigation, we have learned that the fluorination of plastic is commonly used to treat [HYPERLINK "https://pubs.acs.org/doi/10.1021/es1043968"] of polyethylene and polypropylene containers each year ranging from packages consumers handle to larger containers used by retailers such as restaurants and to even larger drums used by manufacturers to store and transport fluids.

Fluorination of plastic and the inadvertent creation of PFAS may be another reason these 'forever chemicals' show up in many unexpected places and is another significant source that must be addressed. Much remains to be resolved as FDA and EPA actively investigate this new source of PFAS; however, preventive steps need to be taken quickly, especially since other PFAS-free barrier [HYPERLINK "https://news.thomasnet.com/fullstory/new-kortrax-barrier-resin-uses-quoral-platform-that-improve-oxygen-transfer-rate-of-hdpe-containers-40019982"] are available as [HYPERLINK "https://www.gantrade.com/faq/evoh-barrier"].

FDA's 1983 approval of fluorine gas treatment of polyethylene

FDA [HYPERLINK "https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=177.1615"], promulgated in 1983, allow the use of fluorine gas to treat polyethylene food-contact articles in amounts that produce up to 5,000 parts per billion (ppb) of total fluorine in the food in the container.[1] The rule indicates that the process affects only the surface of the polyethylene and leaves the interior of the plastic unchanged.

In practice, the [HYPERLINK "https://packagingguruji.com/plastic-fluorination-process/"] substitutes the hydrogen molecules on the plastic's surface with fluorine, effectively creating a barrier to moisture

[1] The regulation uses parts per million. We converted it to parts per billion in order to use a consistent set of units.

and oxygen migration through the polyethylene. The newly created barrier also makes the plastic stronger by preventing the contents from penetrating the plastic and making it softer. We submitted a Freedom of Information Act (FOIA) request to FDA in May to obtain the documents surrounding FDA's 1983 approval and the basis of its determination that the use was safe. We will share more information when we get the agency's response.

What does FDA's limit of 5,000 ppb of extractable total fluorine mean in terms of PFAS levels? Let's use PFOA as an example: PFOA has seven fully fluorinated carbons and a total of 15 fluorine molecules. If all 5,000 ppb of the extractable fluorine was in the form of PFOA, FDA would allow up to 7,260 ppb[2] of PFOA in the food. To provide context, consider a one-liter bottle of fluorinated HDPE where only 1% of the PFAS made from the fluorination process was PFOA; an adult consuming the one-liter of beverage each day would be exposed to more than 300 times the Minimal Risk Level[3] that [HYPERLINK "https://www.fda.gov/food/chemical-contaminants-food/testing-food-pfas-and-assessing-dietary-exposure"] have established for intermediate-duration exposures. And this wouldn't include the risks from other types of PFAS also generated during fluorination or exposures to the substances from other sources.

We have been told by packaging experts and found in marketing materials[4] that fluorination is also used on polypropylene, but we cannot find any FDA approval for the use. If this is happening without an FDA authorization, food manufacturers could be self-certifying the use of fluorine gas as Generally Recognized as Safe (GRAS) without FDA review, a practice that FDA allows and that EDF and Center for Food Safety have challenged in court.

EPA identified eight PFAS from HDPE containers for mosquito control pesticide

After learning that a mosquito spray has PFAS in it, EPA identified the fluorinated HDPE container as a potential source of the contamination and tested various sizes of used and unused containers. In March 2021, EPA [HYPERLINK "https://www.epa.gov/pesticides/rinses-selected-fluorinated-and-non-fluorinated-hdpe-containers"] of its investigation, and confirmed that the fluorination process is what produced the PFAS.

EPA used methanol to rinse eight HDPE containers of 2.5, 30, and 50-gallons in size (representative of the supply chain for pesticides, see the photos below); the alcohol was in contact with the plastic for just one minute. Then it tested the rinsate for PFAS using its [HYPERLINK "https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=343042&Lab=NERL"] and positively

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[2] 7264 µg/kg of food (ppb) = (5000 µg F / kg of food) * (1 µmol F / 19 µg F) * (1 µmol PFOA / 15 µmol F) * (414.07 µg PFOA / µmol PFOA).

[3] Oral Intermediate Minimal Risk Level (MRL) is 3x10-6 miligrams of PFOA per kilogram of body weight per day established by the CDC's Agency for Toxic Substances and Disease Registry in [HYPERLINK "https://www.atsdr.cdc.gov/toxprofiles/tp200.pdf"]. See Table 1-2 and 1-3. FDA [HYPERLINK "https://www.fda.gov/food/chemical-contaminants-food/testing-food-pfas-and-assessing-dietary-exposure"] in June 2021. An Intermediate MRL is based on 15 to 364 days of exposure.

[4] Polypropylene is marketed as a candidate for direct fluorination [HYPERLINK "https://www.berlinpackaging.com/fluorination/"]

identified eight PFAS with carbon-chain lengths between three and ten fully fluorinated carbons, including PFOA.


2.5-gallon jug

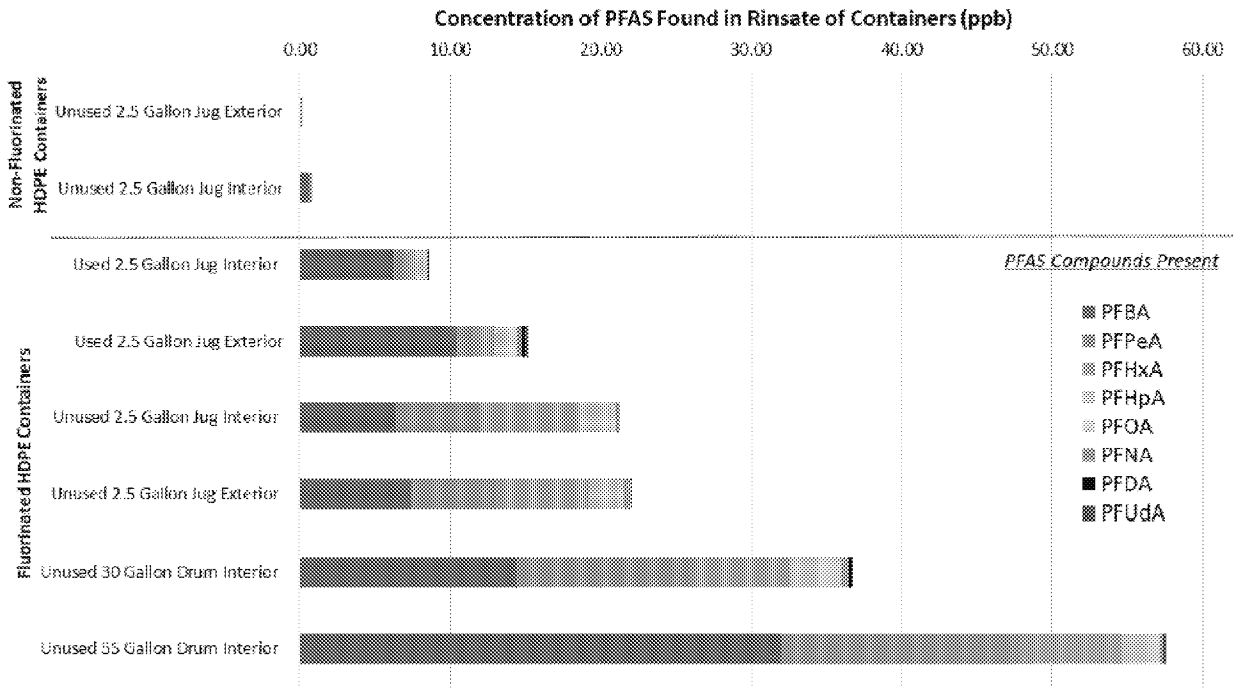

30-gallon drum


55-gallon drum

The total level of the PFAS found ranged from 20-50 ppb in four unused containers; two used containers had lower, but still significant levels. In contrast, the non-fluorinated containers had 1 ppb or less. See the figure below from EPA report for more detail. During this extremely short contact at room temperature, between 1 and 17 micrograms (μg) were extracted in the rinsate. If the contact time and temperature had more closely represented actual conditions of storage and transport, EDF believes the amount extracted would almost certainly have been greater.

Figure 1 shows the average level of PFAS in the rinsates from the non-fluorinated HDPE (top) and the fluorinated HDPE (bottom) containers and indicates that PFAS compounds are more abundant in the fluorinated containers than in the non-fluorinated containers.

Figure 1 - Levels of PFAS in rinsates from containers



In its conclusion, the agency stated that it "believes that through the fluorination process of HDPE containers, PFAS compounds may be formed and then partly leach into the products inside the containers." EPA further explained that:

- During the fluorination process, HDPE containers are subjected to fluorine elemental gas at pre-determined concentrations and under elevated temperatures; and
- The length of time and the conditions under which the product is stored in the fluorinated containers could affect the leaching potential, and consequently the concentration of PFAS found in the products.

EPA also indicated that in future studies it will test these materials under a variety of different conditions including other solvents, different contact times and temperatures and different product storage time to better understand what impact fluorination has on plastic containers and its content.

A 2011 study shows fluorine gas treatment creates PFAS including PFOA

EPA's findings were an affirmation of conclusions previously reached by researchers at the University of Toronto. Amy Rand and Scott Mabury published a [HYPERLINK "https://pubs.acs.org/doi/10.1021/es1043968"] describing how the process of HDPE fluorination effectively generates perfluorinated carboxylic acids, a type of PFAS, of various carbon-chain lengths.

The researchers bought 20 one-liter fluorinated HDPE bottles from two separate firms: Fluoro-Seal International (now [HYPERLINK "https://www.inhancetechnologies.com/"]), which produced bottles with five degrees of fluorination; and Air Products and Chemicals/Airopak which made bottles with only one fluorination level.

After extracting the plastic bottles with methanol at elevated temperatures for two hours, they tested for nine PFAS with fully fluorinated carbon chain lengths between one and nine. The bottles with higher degrees of fluorination (called F5) had the highest amounts of PFAS and the PFAS were longer in length (see table below). Longer PFAS tend to bioaccumulate in the human body longer.

They also stored water in fluorinated bottles for one year and then tested samples of the water for the same PFAS. The average total PFAS was 188 ppb and the PFAS were predominantly short-chain[5]; no PFOA or longer-chain PFAS were detected possibly due to their low affinity for water compared to methanol.

The table below shows that EPA's findings were similar to that from the academic investigators.

Study	Method	Type of fluorinated HDPE container	# PFAS measured	PFAS carbon-chain lengths detected	Estimated PFAS concentration of in contents
EPA	Methanol extraction from plastic; about one-minute rinse	2.5 to 55 gallons	8	4-11	0.05 to 1.2 ppb
Rand and Mabury	Methanol extraction from plastic; 2 hours at 65◦C	1 L with highest fluorination	9	2-10	70 ppb[2]
		1 L with lowest fluorination	9	2-4; 9[1]	5.1 ppb[3]

[1] C5 and 7 were below the limit of quantification; C6,8 and 10 were not detected.
[2] 8.5 ng * 0.5 * 1200 cm^2 inside and outside per kg of contents * 0.001 µg/ng = 5.1 ppb.
[3] 113 ng * 0.5 * 1200 cm^2 inside and outside per kg of contents * 0.001 µg/ng = 70 ppb.

Plastics commonly marketed as fluorinated

Polyethylene and polypropylene[6] are [HYPERLINK "https://www.plasticpackagingfacts.org/plastic-packaging/resins-types-of-packaging/"] in packaging in general and food packaging in particular. High density polyethylene (HDPE) is used in the manufacture of [HYPERLINK

[5] Trifluoroacetic acid (C2) and perfluoropropanoic acid (C3) comprised 80% of the total PFAS. We calculated 188 ppb by multiplying 314 ng/cm2 times 600 cm2 for inside surface of 1L bottle times 1000 ng/microgram.
[6] Polypropylene is not included in FDA's approval of fluorine gas treatment of polyethylene. However, it is marketed as a candidate for direct fluorination [HYPERLINK "https://www.berlinpackaging.com/fluorination/"]

"https://www.plasticpackagingfacts.org/plastic-packaging/resins-types-of-packaging/"] such as milk and non-carbonated beverage bottles, margarine tubs, shampoos and household cleaning products. It is also used to make [HYPERLINK "https://packagingguruji.com/plastic-fluorination-process/"] and intermediate bulk containers used for storage and transportation of food ingredients.

Fluorinated containers are also [HYPERLINK "https://www.mjspackaging.com/blog/when-are-fluorinated-bottles-necessary/"] chemicals that may interact with the plastic including flavors, fragrances, detergent, shampoo and cleaning products, herbicide and insecticides.

Business beware

EPA indicated it has reached out to industry and trade organizations "to raise awareness of this emerging issue and discuss expectations of product stewardship." The presence of PFAS in common plastics has also raised questions about [HYPERLINK "https://business.edf.org/insights/walmart-steps-up-on-recycling-efforts-but-a-gap-remains-in-the-circular-economy-conversation/"] as these types of plastic are [HYPERLINK "https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/plastics-material-specific-data"].

As companies start to phase out PFAS from their products, they should keep in mind that assurances by their suppliers that PFAS are not intentionally used may not be sufficient. Fluorination of plastic surfaces generates PFAS that are likely to leach into the packaging content, but these PFAS are not intentionally used. Companies should ask suppliers whether they fluorinate the plastic containers.

FDA and EPA must address unanswered questions and take action

Given the reported range of products using plastic containers treated with fluorine, we were pleased to see that EPA and FDA are [HYPERLINK "https://www.epa.gov/pesticides/pfas-packaging"] in evaluating the situation and taking the next steps.

We believe that FDA needs to conduct two types of review. The first is whether the product's use is so widespread that it constitutes an [HYPERLINK "https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?CFRPart=2&showFR=1"] that poses a significant threat of danger that should be corrected immediately to prevent injury. To do this assessment, FDA should work with EPA to quickly identify and investigate container manufacturing facilities that store significant quantities of fluorine gas and have had to submit [HYPERLINK "https://www.epa.gov/rmp"] under the Clean Air Act.

The second is whether there is sufficient evidence that the fluorine gas treatment approved by the [HYPERLINK "https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=177.1615"] for polyethylene is safe to allow its continued use as a food contact substance. For this purpose, [HYPERLINK "https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=170.3"] defines safe to mean "there is a reasonable certainty in the minds of competent scientists that the substance is not harmful under the conditions of its intended use" after considering three factors that include "the cumulative effect of the substance in the diet, taking into account any chemically or pharmacologically related substance or substances in such diet."

Given the evidence we see from EPA 2021 study and Rand and Mabury's 2011 study, we cannot see how FDA could maintain the fluorination treatment process is safe.

We have written extensively about the use of PFAS to grease-proof paper-based food packaging and their risk to health [HYPERLINK "http://blogs.edf.org/health/2020/04/01/fda-scientists-push-back-industry-analysis-pfas/"], [HYPERLINK "http://blogs.edf.org/health/2020/08/04/fda-phasing-out-paper-greaseproofing-pfas/"] and [HYPERLINK "http://blogs.edf.org/health/2021/05/13/the-chemical-industry-hid-evidence-of-harm-from-pfas-3-takeaways/"]. The new EPA investigation raises additional questions about potential food contamination from plastic sources.